



Work, Heat and Energy

The Web Site is Now Up! Latest schedules and assignments will be posted there

Grade Policy: Final grading will be done on a curve.

Tutors:

The GSI's are there to help! Use them!

There may be some help available at the Student Learning Center

<http://www-slc.uga.berkeley.edu:80/>

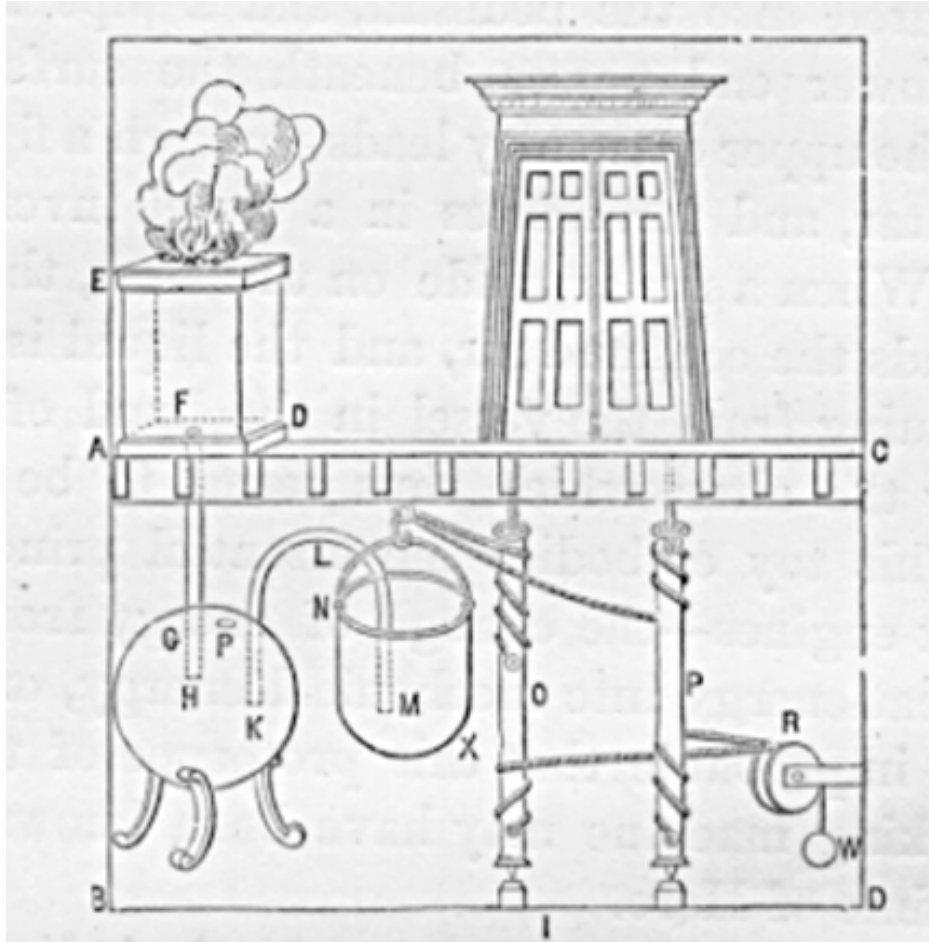
Look around on bulletin boards.

Web:

I will try and post lectures the night before they are given. But no promises.

Tests: Vote! If you have them, the exams will be adjusted accordingly!

Thermodynamics and a Little History



Thermodynamics is the study of patterns of energy change.

In the temple door steam engine we convert

Chemical energy to heat

Heat to gas expansion

Expansion to liquid displacement

Displacement to mechanical work

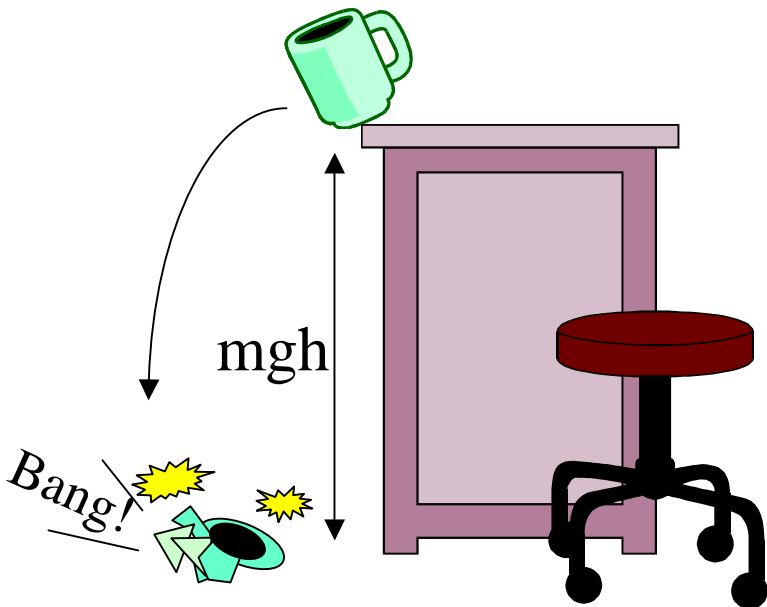
About 2/3 of the course will be dedicated to studying these patterns.

Work, Heat and Energy

More specifically, chemical thermodynamics deals with:

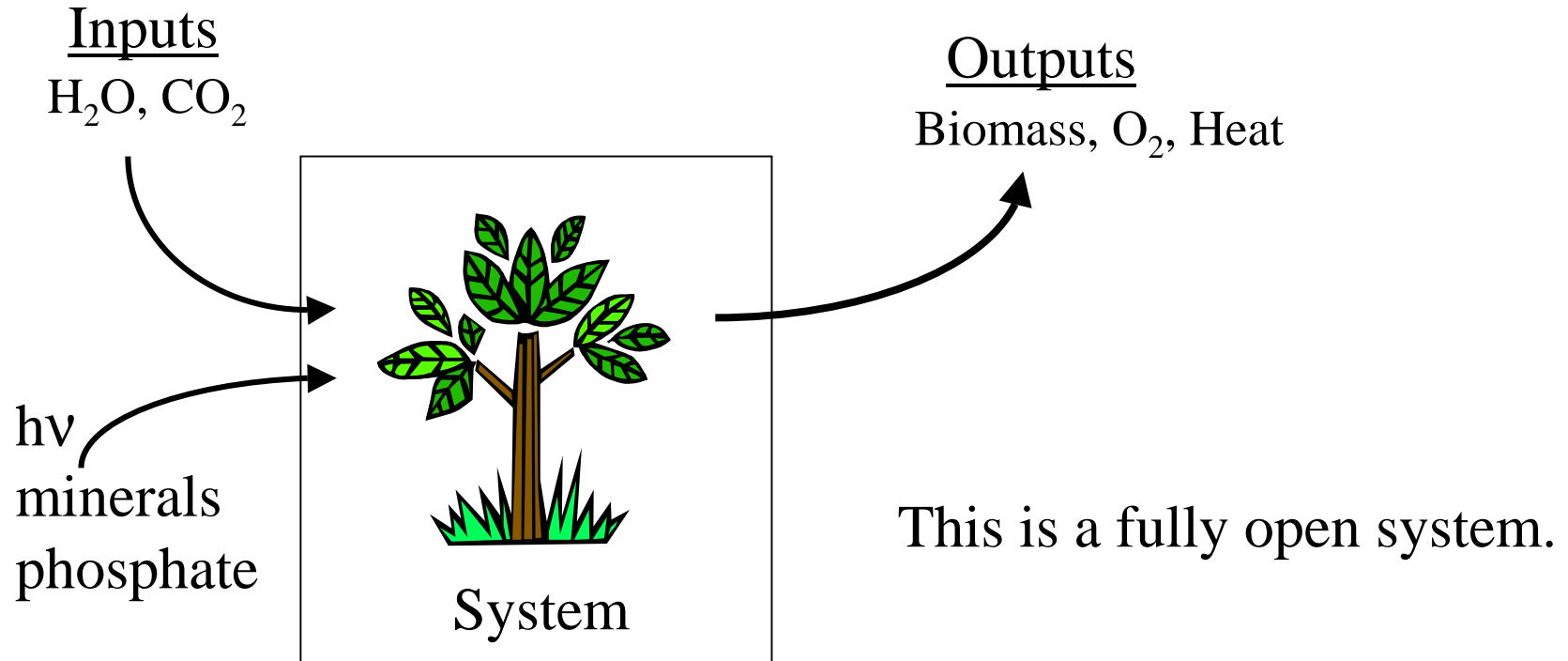
- Energy Conversion
- Molecular Stability
- Direction of change

Examples

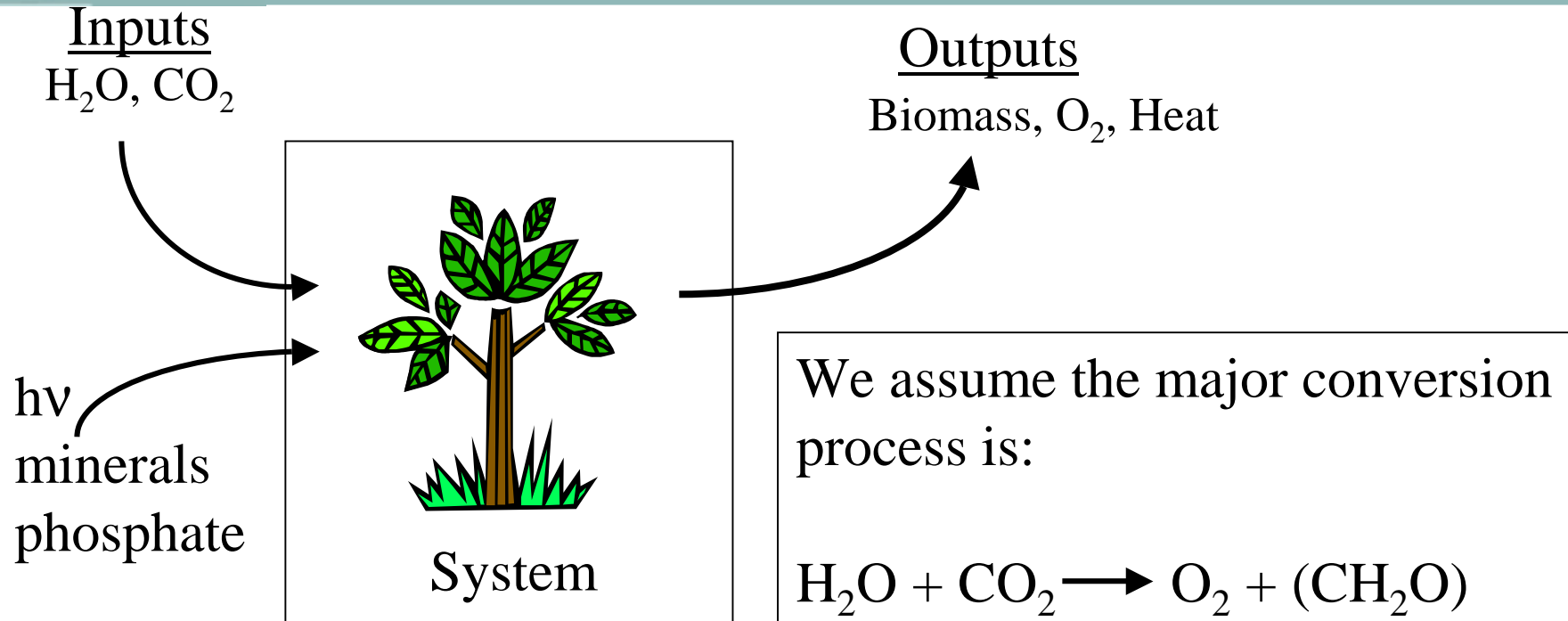


Thermodynamics and Photosynthesis

As a more complex example consider photosynthesis. _____



Thermodynamics and Photosynthesis



The enthalpy change for the process is $\Delta H^\circ = 485 \text{ Joules/mol}$

In order to get this process to go we need: light, and a catalytic system. This takes place in the chloroplast of the plant.



Photosynthesis and Efficiency

We assume the major conversion process is:



It has been shown that it takes about 8-9 photons to make one O_2 .

The first law tells us that the total energy input must equal total energy output.

Photon Energy = Chemical Energy + Heat

Efficiency = Chemical Energy / Photon Energy



Photosynthesis and Efficiency

So to calculate the efficiency of production of 1 mole of O₂:

1 mole of photons = 1 einstein

Photon Energy = (8-9 einsteins)(6*10²³ photons/mol) $h\nu$

h = planck's constant = 6*10⁻³⁴ Js

$\nu = c/\lambda = (3*10^8 \text{ m/s}) / (680*10^{-9} \text{ m})$

Photon Energy = 1400-1570 kJ

Chemical Energy = 485 kJ/mol * 1 mol O₂

%Efficiency = 485/1570 * 100 = 31%



Work, Heat and Energy

Let's be more precise about different forms of energy:

Heat is the exchange of energy from a hot body to a cold one.

Work involves the net movement of matter from one location to another.

We will be studying many forms of work in this course:

- Pressure/Volume work

- Electrical Work

- Mechanical Work



Work: Definition and Example

Work is a force times a distance. In equation form:

$$w = \int f_{ex} dx$$

f_{ex} = external force, dx = displacement

Pressure/Volume Work:

$$w = - \int P dV$$

P = opposing pressure, dV = Volume change

Spring Extension and Compression

$$w = k \int (x - x_0) d(x - x_0)$$

k = Hooke's law constant

Gravitational Work

$$w = mg \int dh$$

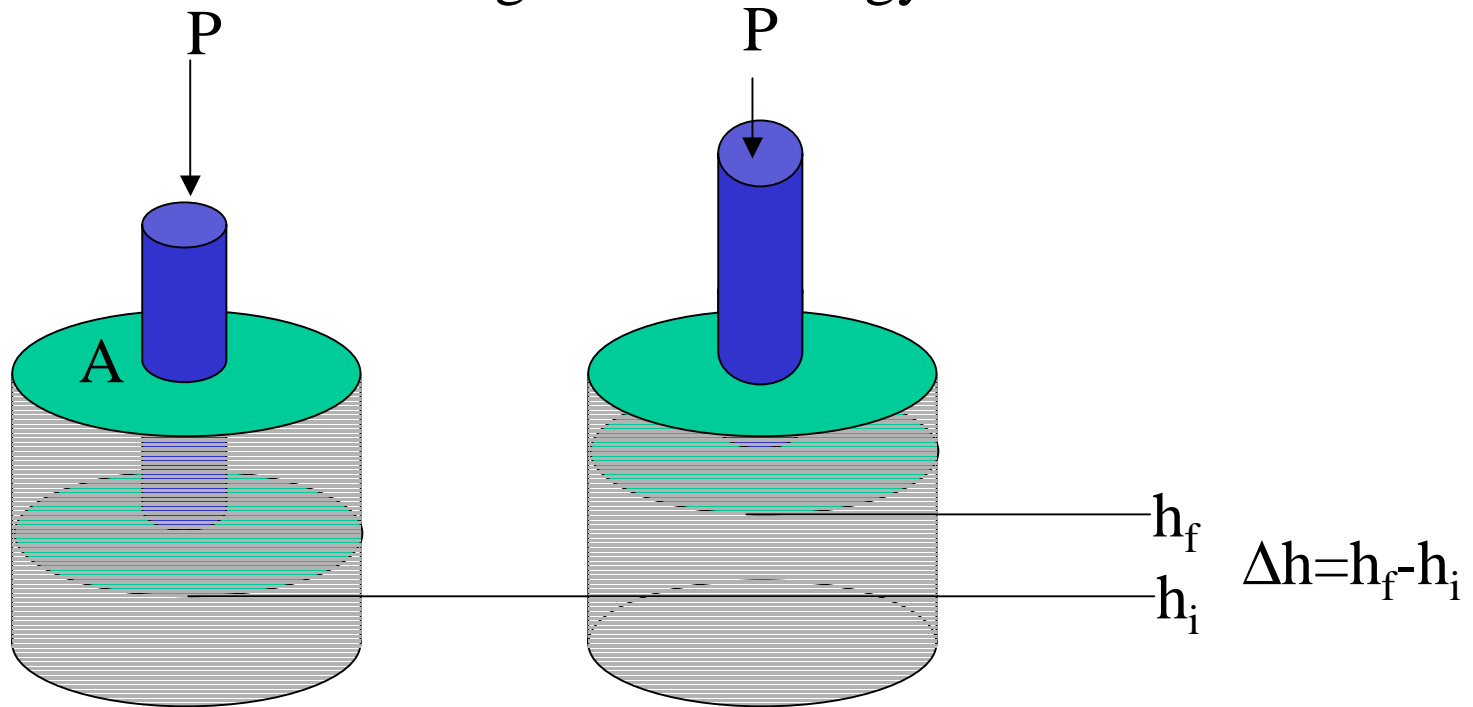
m = mass, g = gravitational constant
 h = height

Pressure Volume Work

Expansion under constant pressure: $w = -P\Delta V = -PA\Delta h$

Since Δh is positive the work is negative.

System works on surroundings-- loses energy.



So the work done by expansion of a 1 liter of a gas to 2 liters against a constant pressure at 10 atm is: $w_p = -P_{\text{ex}} (V_2 - V_1) = -10 \text{ atm} * 1 \text{ liter}$
 $w_p = -10 \text{ liter} * \text{atm} (101.3 \text{ J/L} \cdot \text{atm}) = -1013 \text{ Joules}$



Heat and Heat Capacity

We denote the heat transferred between system and surrounding by q .

Heat moves from a hotter body to a cooler one. At equilibrium these bodies will be at the same temperature.

Different materials will have different capacities for giving up or taking in heat. (Why?)

The formal definition of heat capacity, C , is:

The amount of thermal energy that must be added to a system per unit temperature rise under specific conditions.

$$C = \frac{dq}{dT}$$

Or equivalently

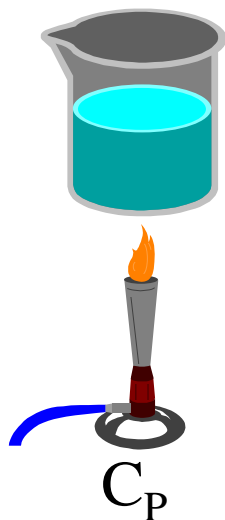
$$q = \int C dT$$

Different Heat Capacities

The ability of a material to transfer heat depends on the conditions.

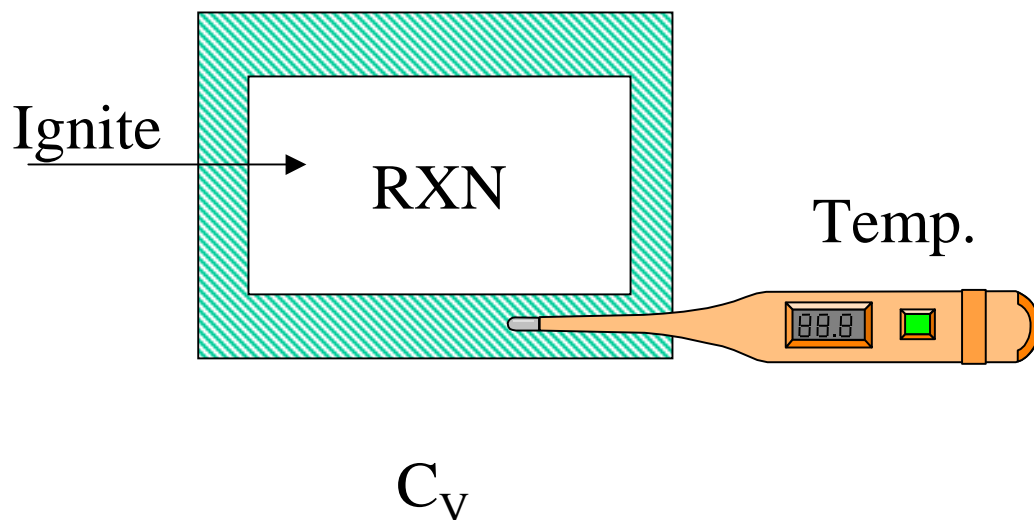
For examples, processes can be carried out at constant volume or constant pressure.

Bench Chemistry



Constant Pressure Process(isobaric)

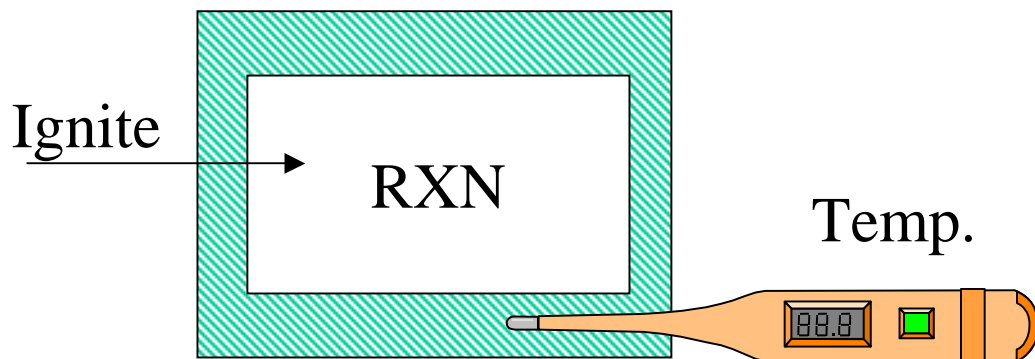
Bomb Calorimetry



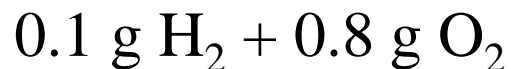
Constant Volume Process (isochoric)

Heat Capacity is an extensive property. To compare capacities we use molar heat capacities or specific heat capacities.

Bomb Calorimetry



Consider the system:



We find that the heat capacity at constant volume for this amount of material is $C_v = 21,700 \text{ calories/}^\circ\text{C}$.

After ignition we find that the temperature has risen from 25°C to 25.155°C

$$q_v = C_v \cdot \Delta T = 21,700 \text{ cal/}^\circ\text{C} \cdot (0.155^\circ\text{C}) = 3360 \text{ cal}$$

But remember we choose the sign such that heat evolved by the system is negative! So really: $q_v = -3.36 \text{ kcal}$



Equations of State

An equation of state relates the variables of state (P,V,T,n).

Let's consider equations for volume.

In solids and liquids

$$dV/dP \cong 0,$$

$$dV/dT \cong 0$$

$$V(T,P) \cong \text{constant}$$

In gases:

e.g. An ideal gas--

$$V(T,P,n) = (nRT)/P$$

e.g. A van der Waals gas

$$\left(P + \frac{n^2 a}{V^2}\right)(V - nb) = nRT$$



State Changes

Now that we have an understanding of

- 1) What kinds of energy can be transferred
- 2) What kinds of equations define the state of a system.

How do we treat changes between states?

Changes include not only the heat and work, temperature and pressure with which we are now familiar but also changes in physical and chemical states.

We will use two concepts:

Internal Energy, E and Enthalpy, H

to describe these changes.



Energy and Enthalpy

Types of energy that can be transferred:

Heat

Work

We are interested in measures of the energy of our system.

Remember heat and work are path dependent.

Energy (E)- Energy is the capacity for doing work.

Enthalpy (H)- The heat content of a system. (Really, $E + PV$)

Thus enthalpy is really an energy corrected for the pressure/volume work.

E and H are variables of state.

Introduction to the First Law

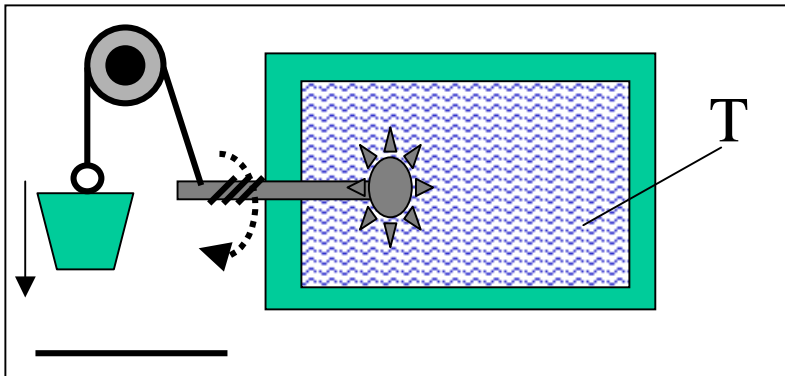
The state of system changes when heat is transferred to or from the system or work is done.

If these are the only forms of energy in the system (e.g. no mass is transferred) then it seems reasonable that energy must be conserved!

$$E_2 - E_1 = q + w \quad (\text{with the proper sign conventions})$$

But it was not obvious early on that this “Law” held.

Joule in around 1843 did the definitive experiment:



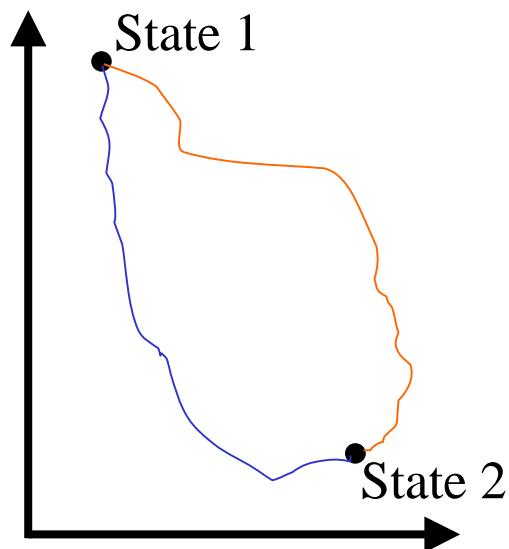
Essentially, the amount of heat generated in the vessel by the movement of the paddle is exactly the potential energy lost by the weight.



In a public lecture, Joule rejoiced in this understanding: "...the phenomena of nature, whether mechanical, chemical or vital, consist almost entirely in a continual conversion of attraction through space [PE], living force [KE], and heat into one another. Thus it is that order is maintained in the universe-nothing is deranged, nothing ever lost, but the entire machinery, complicated as it is, works smoothly and harmoniously. ...every thing may appear complicated and involved in the apparent confusion and intricacy of an almost endless variety of causes, effects, conversions, and arrangements, yet is the most perfect regularity preserved...."



Path dependence and independence



q and w are path dependent variables.

A state change that occurs over the blue path has q_{blue} , w_{blue} .

Over the red path we get q_{red} , w_{red} .

All we know from the 1st Law is

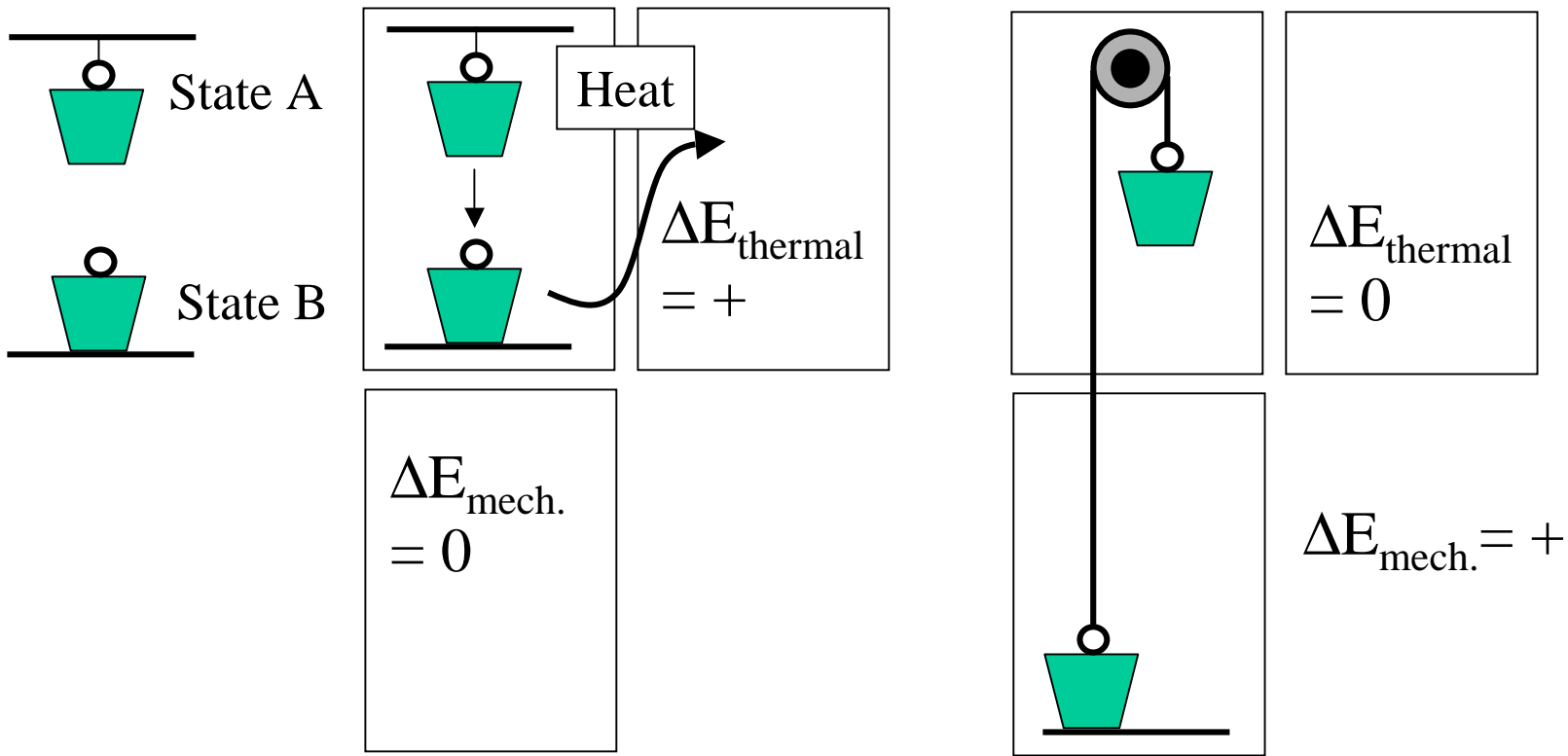
$$q_{\text{blue}} + w_{\text{blue}} = q_{\text{red}} + w_{\text{red}}$$

Reversibility of Paths: Mechanical Work

States may be changed either reversibly or irreversibly.

Reversible: State is changed by differential amounts along a path. At any moment a small change in the opposing force will alter the direction of the state change.

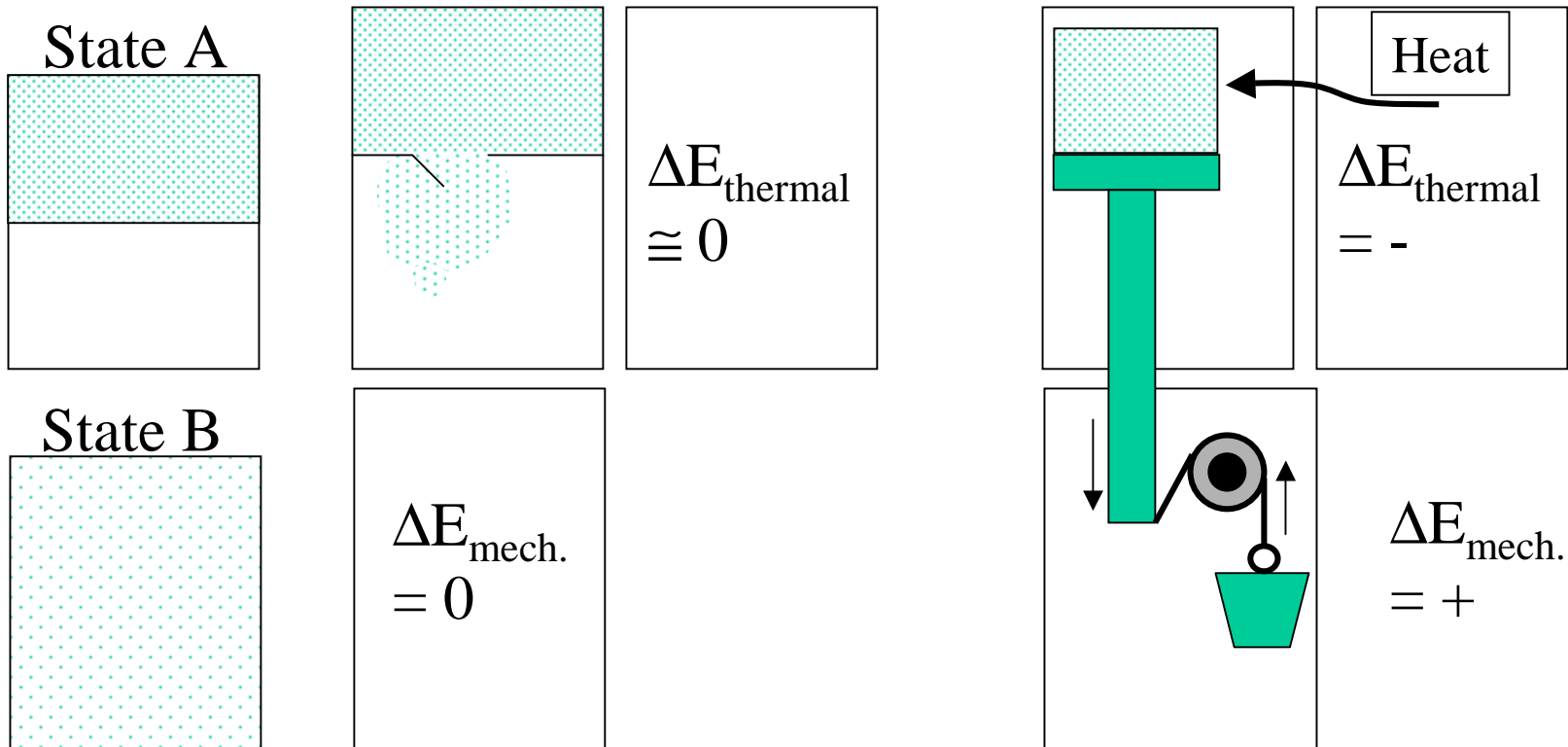
Irreversible: “All at once”-- the method of the change is such that it is not possible to reverse the direction.



Reversibility of Paths: PV Work

Here in the irreversible case you would have to do significant mechanical work to restore the initial state.

In the reversible case, a small differential change in the weight can cause a reversal.



Temperature and Pressure Changes

How does ΔE change with temperature?

Liquids and solids:

$$\text{Constant P: } q = \int C_P dT = C_P \Delta T; w = 0 \qquad \Delta E = q + w = C_P \Delta T$$

$$\text{Constant V: } q = \int C_V dT = C_V \Delta T; w = 0 \qquad \Delta E = q + w = C_V \Delta T$$

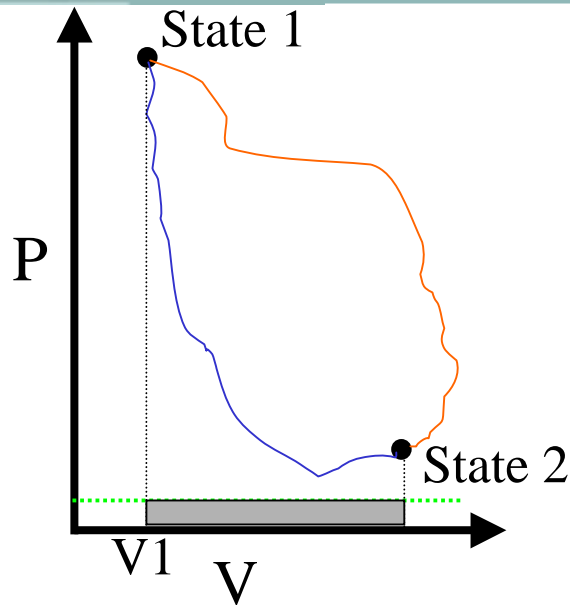
Gases:

$$\text{Constant P: } q = \int C_P dT = C_P \Delta T; w = -P_{ex} \Delta V$$

$$\text{Constant V: } q = \int C_V dT = C_V \Delta T; w = 0$$

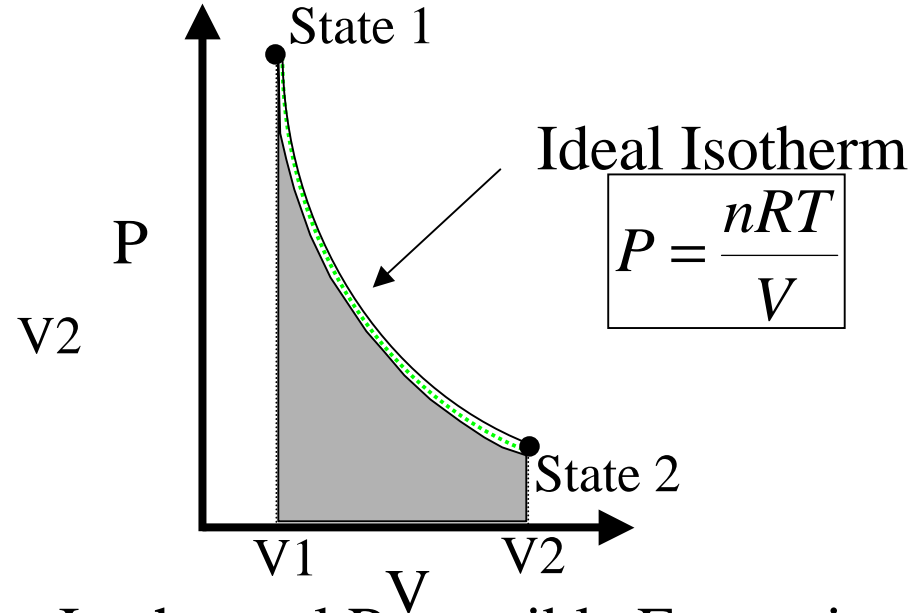
$$\text{Constant T: } w = -\int P_{ex} dV = -\int P_{in} dV = -\int \frac{nRT}{V} dV = -nRT \ln\left(\frac{V_2}{V_1}\right)$$

Work obtained from reversible vs. irreversible processes



Constant Pressure Expansions

- 1) $P_{\text{op}} = 0$ implies $w=0$ thus $\Delta E=q$
- 2) $P_{\text{op}} = \text{Const.}$ implies $w=P_{\text{op}} \Delta V$



Isothermal Reversible Expansion

$T=\text{Const.}, P_{\text{op}} \cong P_{\text{gas}}, n=\text{Const.}$

$$w = - \int_{V1}^{V2} \frac{nRT}{V} dV = -nRT \int_{V1}^{V2} \frac{dV}{V}$$

$$w = -nRT [\ln(V2) - \ln(V1)]$$

$$w = -nRT \ln\left(\frac{V2}{V1}\right)$$



Next Time

Other sorts of changes include:

Physical changes

fusion (melting)	= solid	to	liquid
freezing	= liquid	to	solid
vaporization	= liquid	to	gas
condensation	= gas	to	liquid
sublimation	= solid	to	gas

Chemical changes

Overall chemical reactions
Breaking of molecular bonds



Homework

Due *Friday* at discussion section.

- 1) (a) The enthalpy of unfolding of HIV protease is 50 kcal/mol at 50 °C and 80 kcal/mol at 70 °C . Estimate the ΔC_p for the unfolding of this protein, assuming ΔC_p is a constant over this temperature range. (b) The heat capacity of unfolded (denatured) proteins is generally found to be higher for the same proteins in their native state. Can you think of a reason for this observation?
- 2) A biochemist decided to measure the heat of oxidizing sucrose to CO_2 and water (l) by allowing sugar to be metabolized by bacteria. The find a heat evolution of 400 kcal/mol of sucrose. Compare this value with the standard enthalpies from the tables in your textbook. Can you identify the erroneous assumption in the design of the experiment?
- 3) Calculate the work done in the reversible adiabatic expansion of one mole of an ideal monotonic gas from 10 atm to 1 atm, starting at 300K.
- 4) TSW Problems 2.2, 2.3, 2.8, 2.17, 2.19